Anal. Calcd for $C_8H_7Cl_5$: C, 34.26; H, 2.52. Found: C, 34.30; H, 2.78.

1,2,3,4-*syn*-7-Pentachloro-5-*exo*-methylbicyclo[2.2.1]-2-heptene (24c), a colorless liquid, was the second compound eluted (162 min retention time, 57.0%). The compound has $\lambda_{max}^{CS_2}$ 6.30, 7.80, 7.88, 9.91, 10.05, 10.51, 11.40, 12.21, 13.89 μ; nmr δ 1.04 (methyl, 3 H doublet, J = 6.59 Hz), 1.67 (1 H multiplet), 2.52 (broad, 2 H multiplet), 4.21 (*anti*-7, sharp 1 H singlet).

Anal. Calcd for $C_8H_7Cl_5$: C, 34.26; H, 2.52. Found: C, 34.25; H, 2.55.

1-Bromo-1,2,3,4,5-pentachloro-2,4-cyclopentadiene (27) was prepared according to the procedure of Mark.[36]

Phosphorus tribromide, 108 g (0.40 mole), and hexachlorocyclopentadiene, 328 g (1.20 moles), were heated in a 500-ml three-necked flask equipped with magnetic stirrer, thermometer, and fractional distillation head. Heating was adjusted so that the pot temperature reached 160° in 4 hr and was maintained between 160 and 164°. After 7 hr at this temperature a deep red liquid (81 g) was slowly distilled from the reaction mixture between 70 and 80° over 9 hr. The contents of the reaction flask were then distilled to give unreacted hexachlorocyclopentadiene, bp 59–65° (0.25–0.30 mm), and a mixture of **27** and the hexachloro compound, bp 68–99° (0.20–0.30 mm). This was redistilled through a 10-in. Vigreux column, then twice distilled through a spinning-band distillation column, and finally through the Vigreux column again (bp 60° (0.15 mm), $n^{25}D$ 1.5870) to give 40 g (8.4% yield of **27**). Glpc (SF-96 column, 175°) indicated the purity of **27** was 99%. The reported yield is 22%, bp 43–44° (0.04 mm), $n^{25}D$ 1.5880.[36]

Reaction of 27 with Maleic Anhydride. A solution of 1.42 g (4.50 mmoles) of **27** and 0.32 g (3.25 mmoles) of maleic anhydride in 4 ml of nitrobenzene was heated for 14 hr at 136°. Completion of the reaction was indicated by the disappearance of the 12.0-μ maleic anhydride band in the infrared spectrum. Glpc (SF-96 column, 210°) showed only one peak which was collected as crystals, mp 230–250° (evacuated capillary). The nmr spectrum of this white solid was identical with that of the crude reaction mixture; it consists of two singlets at 4.19 and 4.24 ppm and four doublets at 4.07, 4.15, 4.18, and 4.26 ppm of which the first two had splittings of 2.40 Hz and the last two of 2.10 Hz. The intensity of the singlet at 4.19 ppm showed that it comprised about 50% of the isomeric mixture. The infrared spectrum of the white crystals in $CHCl_3$ was simple and had prominent peaks at 5.36, 5.60, 6.30, 9.41, 10.71, and 11.19 μ.

Anal. Calcd for $C_9H_2O_3BrCl_5$: C, 26.03; H, 0.49; Br, 19.24; Cl, 42.68. Found: C, 25.96; H, 0.44; Br, 19.06; Cl, 42.45.

Dimerization of 9. The dimerization of **9** (30% in CS_2, room temperature) was shown by the disappearance of the singlet at 4.73 ppm and the growth of two new singlets of equal intensity at 4.86 and 4.96 ppm ($W(h/2)$ = 0.2 Hz). The dimer has mp 221°; $\lambda_{max}^{CS_2}$ 6.25, 8.13, 8.31, 9.68, 10.37, 11.48, 12.60, 13.91 μ. The ultraviolet spectrum shows $\lambda_{max}^{CHCl_3}$ 249 mμ (ϵ = 760). Only one peak was detected on glpc (SE-30 column, 200°).

1,2,3,4,5,6,7,8,9,10-Decachloropentacyclo$[5.2.1.0^{2,6}.0^{3,9}.0^{4,8}]$decane (35 or 36) was prepared by irradiating a solution of 11.90 g (25 mmoles) of the dimer of **9** in 150 ml of acetone for 2 hr with a 450-W Hanovia lamp in a quartz apparatus. Completion of the reaction was indicated by disappearance of the double bond peak at 6.26 μ in the infrared spectrum. Removal of the acetone *in vacuo* gave a dark brown residue which was sublimed at 200° (1 mm) to give 9.41 g (79% yield) of white gummy crystals. A sample for analysis was further purified by elution through an alumina column with low boiling ligroine and crystallizations from a 7:1 ethanol–water mixture. The melting point taken in an evacuated capillary in an aluminum block was 372° dec. The nmr spectrum shows only a sharp singlet at 4.56 ppm ($W(h/2)$ = 0.3 Hz) for the two protons of **35** or **36**. The infrared spectrum has $\lambda_{max}^{CS_2}$ 7.93, 8.12, 8.46, 8.82, 9.04, 9.33, 9.90, 11.56, 11.88, 12.67, 13.02, 13.42 μ.

Anal. Calcd for $C_{10}H_2Cl_{10}$: C, 25.20; H, 0.42. Found: C, 25.02; H, 0.48.

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The Stereospecific Syntheses of Ferrocene Derivatives with Leaving Groups β to the Metallocene

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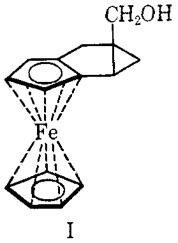
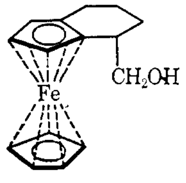
Abstract: The stereospecific syntheses of *exo*- and *endo*-α-hydroxymethyl-1,2-tetramethyleneferrocene (I and II, respectively) are discussed. The stereospecific generation of the *endo* isomer (II) results from the addition of the hydrogen of disiamylborane to α-methylene-1,2-tetramethyleneferrocene (VIII) exclusively from the *exo* direction. The exclusive neutralization of α-metallocenyl carbonium ions by *exo* attack of a nucleophile provides a stereospecific route to the *exo* isomer (I).

In connection with a continuing interest in metallocenyl carbonium ions[1-3] *exo*- and *endo*-α-tosyloxymethyl-1,2-tetramethyleneferrocene (the tosylates of I and II) were required for solvolytic studies. The stereospecific synthesis of these two isomers was therefore undertaken and forms the subject of this paper.



I



II

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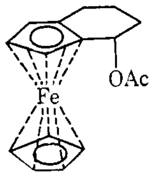
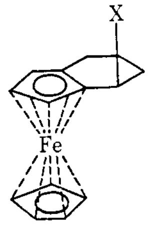
[1] J. H. Richards and E. A. Hill, *J. Am. Chem. Soc.*, **81**, 3483 (1959).
[2] E. A. Hill and J. H. Richards, *ibid.*, **83**, 3840 (1961).
[3] E. A. Hill and J. H. Richards, *ibid.*, **83**, 4216 (1961).

Results

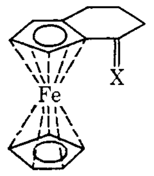
The *exo* isomer was prepared by treatment of *endo*-α-acetoxy-1,2-tetramethyleneferrocene (III) with sodium cyanide in methanol. Basic hydrolysis of the resulting nitrile IV to the carboxylic acid V, and esterification of VI by methanolic hydrochloric acid in the presence of zinc amalgam to prevent the oxidative decomposition of the ferrocene nucleus, followed by reduction with lithium aluminum hydride, afforded the *exo* alcohol I. The intermediate nitrile, acid, and ester are unstable and so were not extensively purified.


III


IV, X = -CN
V, X = -CO_2H
VI, X = -CO_2CH_3

The *exo* stereochemistry of the alcohol is confirmed by infrared spectral analysis. Thus, a dilute solution (0.005 *M*) of the alcohol in carbon tetrachloride shows absorption in the hydroxyl region only at 3645 and 3610 cm^{-1}. These absorptions have been assigned respectively to a free hydroxyl group and a hydroxyl group hydrogen bonded to the π-electron system of the cyclopentadienyl ring of ferrocene;[4] there is no absorption due to a hydroxyl group which is hydrogen bonded to the central metal.

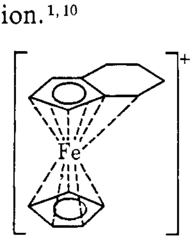
Synthesis of the *endo* isomer II began with α-keto-1,2-tetramethyleneferrocene (VII)[3] which reacted smoothly with triphenylmethylenephosphorane in dimethyl sulfoxide[5] to give consistently good yields (73%) of α-methylene-1,2-tetramethyleneferrocene (VIII). Hydroboration of this olefin with disiamylborane in tetrahydrofuran[6,7] followed by oxidation with hydrogen peroxide provided the *endo* alcohols with high stereospecific control.


VII, X = =O
VIII, X = =CH_2

The stereochemistry of the *endo* isomer was also confirmed by its infrared spectrum; a dilute solution (0.005 *M*) in carbon tetrachloride shows absorption only at 3643 and 3527 cm^{-1}. The former band is due to a free hydroxyl group; the latter arises from a hydroxyl group hydrogen bonded to the iron atom.[3,4] In this isomer no absorption due to a hydroxyl hydrogen bonded to the π electrons of the cyclopentadienyl ring is observed; such hydrogen bonding is geometrically impossible in the *endo* isomer. Interestingly, though there is a large shift ($\Delta\nu$ = 116 cm^{-1}) between the free hydroxyl and the one hydrogen bonded to the iron, the relative intensity of these two absorptions indicates that only about 60% of the alcohol is hydrogen bonded. The large shift implies that the enthalpy of hydrogen bonding is more favorable[8] than in other cases in which hydroxyl groups are completely hydrogen bonded (*e.g.*, α-hydroxyl-1,2-tetramethyleneferrocene,[3] $\Delta\nu$ = 49 cm^{-1}). This is undoubtedly due to the loss in entropy in the hydrogen bonded form in which the rotational freedom of two bonds (the carbon–carbon bond and the carbon–oxygen bond) has been lost.

Discussion

The stereospecific synthesis of the *exo* alcohol I results from the exclusive attack of cyanide ion on the acetate III to produce α-cyano-1,2-tetramethyleneferrocene. This can be due either to an SN2 attack by cyanide on the acetate or, more probably, be the result of neutralization of the α-ferrocenyl carbonium ion IX from the *exo* direction.[1,10]


IX

Stereospecific synthesis of *endo*-α-hydroxymethyl-1,2-tetramethyleneferrocene may be explained in terms of stereoselectivity of disiamylborane[11] which approaches the methylene group from the sterically less hindered *exo* direction so that as the carbon α to the ferrocene changes from a trigonal to tetrahedral configuration; the hydrogen occupies the *exo* location, giving rise eventually to α-*endo*-hydroxymethyl-1,2-tetramethyleneferrocene.

The tosylates of the *exo* and *endo* alcohols (I and II, respectively) both melt sharply at 100–101°; however, the melting point of a mixture of the two isomers is depressed by 20° and occurs over a wide range. The *endo*-tosylate is so reactive that a satisfactory analysis was never obtained, though the benzoate ester gave a good analysis.

Experimental Section

α-*exo*-Carbomethoxy-1,2-tetramethyleneferrocene (VI). Crude α-*endo*-acetoxy-1,2-tetramethyleneferrocene[3] (5.05 g, 16.9 mmoles) was dissolved in 270 ml of methanol contained in a three-necked flask. The flask was equipped with a magnetic stirrer, a reflux condenser, and a nitrogen inlet. After the addition of 50.5 g (1.030 moles) of freshly opened sodium cyanide, nitrogen was bubbled through the solution for 10 min. The solution was then refluxed under nitrogen for 7 hr. The nitrile (IV) thus formed was hydrolyzed by the addition of 17 g (420 mmoles) of sodium hy-

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(4) D. S. Trifan and R. Backsai, *J. Am. Chem. Soc.*, **82**, 5010 (1960).

(5) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

(6) G. Zweifel, K. Nagase, and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 190 (1962).

(7) H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961).

(8) According to Badger's rule,[9] the energy of a hydrogen bond is proportional to the frequency shift of the OH stretching frequency; *cf. e.g.*, L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 490–495.

(9) R. M. Badger, *J. Chem. Phys.*, **5**, 837 (1937).

(10) D. S. Trifan and R. Backsai, *Tetrahedron Letters*, No. 13, 1 (1960).

(11) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

droxide and refluxing for 10 hr. The aqueous solution was cooled, washed three times with ether, and then added to a mixture of 50 g of 10% zinc amalgam, 333 ml of concentrated hydrochloric acid, 333 ml of methanol, and 250 ml of benzene. Hydrogen cyanide was evolved during this addition. The reaction mixture was refluxed until the aqueous layer was colorless. The benzene layer was extracted and washed three times with water. Benzene was removed at reduced pressure, and the resulting brown oil was chromatographed on grade III neutral alumina. The ester was eluted with benzene–hexane in 65% yield. This ester decomposed on standing or when dissolved in chlorinated solvents.

α-*exo*-**Hydroxymethyl-1,2-tetramethyleneferrocene** (I). α-*exo*-Carbomethoxy-1,2-tetramethyleneferrocene (VI) (10 g, 33.6 mmoles) was reduced with lithium aluminum hydride. After a 20-min period, water was added and the solution was filtered and dried over sodium sulfate. Evaporation of ether produced a brown oil which was chromatographed on grade III neutral alumina. The alcohol, *exo*-α-hydroxymethyl-1,2-tetramethyleneferrocene, was eluted with 1:1 methylene chloride–hexane in 25% yield. The infrared spectrum of a dilute solution of the alcohol in carbon tetrachloride (0.005 *M*) showed absorption at 3645 and 3610 cm^{-1}.

α-*exo*-**Tosyloxymethyl-1,2-tetramethyleneferrocene.** The tosylate was prepared by dissolving equivalent amounts of α-*exo*-hydroxymethyl-1,2-tetramethyleneferrocene and recrystallized *p*-toluenesulfonyl chloride in excess pyridine that had been dried over barium oxide. The reaction was allowed to proceed overnight at 0°. The reaction mixture was then poured into a mixture of chloroform, ice, and concentrated phosphoric acid. The organic layer was extracted, and washed three times with water. After drying the product mixture over sodium sulfate, the chloroform was evaporated at reduced pressure. The resulting oil was dissolved in ether–hexane and recrystallized at −77°. The crystals thus obtained were used to seed the mother liquor so that further low-temperature crystallization was unnecessary. The *exo*-tosylate, obtained in 49% yield, melted at 100–101°.

Anal. Calcd for $C_{22}H_{24}O_3FeS$: C, 62.27; H, 5.70; Fe, 13.16. Found: C, 62.30; H, 5.96; Fe, 13.36.

α-**Methylene-1,2-tetramethyleneferrocene (VIII).** A solution of 1.0 g (3.9 mmoles) of α-keto-1,2-tetramethyleneferrocene in 8 ml of dimethyl sulfoxide was added to 7.8 mmoles of the triphenylmethylenephosphorane in dimethyl sulfoxide[5] maintained at room temperature in a purified nitrogen atmosphere. The reaction mixture was stirred for 20 hr at room temperature and then poured into 100 ml of water. The resulting aqueous solution was extracted until the ethereal extract was nearly colorless. The extract was then washed four times with water and dried over anhydrous sodium sulfate. The dark oil, obtained after evaporation of the ether, was chromatographed on grade III neutral alumina. The olefin was eluted with hexane as an orange oil in 73% yield. A second band, which was eluted with 1:4 methylene chloride–hexane, proved to be the starting ketone, 25% of which was thus recovered. The infrared spectra of the product olefin had absorptions at 1630 cm^{-1} (conjugated olefin) and 1228 cm^{-1} (methylene deformation). The ultraviolet spectrum showed λ_{max} at 278 and 450 mμ, which are similar to those reported for vinylferrocene.[12] Attempted vacuum distillation of this material resulted in extensive decomposition.

α-*endo*-**Hydroxymethyl-1,2-tetramethyleneferrocene (II).** Disiamylborane (61.2 mmoles) was prepared according to the external generation method.[5,7] A solution of 5.15 g (20.4 mmoles) of α-methylene-1,2-tetramethyleneferrocene (VIII) was added *via* syringe to disiamylborane in 15 ml of tetrahydrofuran at 0°. The stirred reaction mixture was maintained in a purified nitrogen atmosphere for 24 hr, after which 15 ml of water was added. Sodium hydroxide (22 ml of a 3 *N* solution) was then added followed by the careful addition of 22 ml of 30% hydrogen peroxide. The organic layer was then extracted and washed three times with water. After drying the organic extract with sodium sulfate, the ether was removed at reduced pressure and the residue chromatographed on grade III, neutral alumina. The *endo* alcohol was obtained as an oil in 47% yield (2.6 g) together with 1.2 g (23%) of the starting olefin. The nmr spectrum of this material was very similar to that described for the *exo* isomer (I). The infrared spectrum of a dilute solution of the *endo* alcohol in carbon tetrachloride (0.005 *M*) showed absorption at 3643 and 3527 cm^{-1}.

α-*endo*-**Tosyloxymethyl-1,2-tetramethyleneferrocene** was prepared according to the procedure described above for the *exo*-tosylate. The yellow tosylate, which was obtained in 66% yield, melted at 100–101° in a sealed, evacuated capillary.

α-*endo*-**Benzoxymethyl-1,2-tetramethyleneferrocene** was obtained by dissolving 100 mg (0.37 mmole) of α-*endo*-hydroxymethyl-1,2-tetramethyleneferrocene (II) in 2 ml of benzoyl chloride and 0.5 ml of pyridine. After 10 min at room temperature, the reaction mixture was chromatographed on grade III neutral alumina; the ester was eluted with hexane as a brown oil. Low-temperature (−77°) crystallization from hexane produced yellow needles that were then used to seed solutions which were then crystallized in the normal manner. Three recrystallizations produced the benzoate ester in 44% yield, mp 80–81.5°.

Anal. Calcd for $C_{22}H_{22}O_2Fe$: C, 70.60; H, 5.93. Found: C, 70.51; H, 5.72.

Acknowledgment. This work was supported by the National Science Foundation, NSF GP-24996 and the Paint Research Institute.

[12] F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, 77, 6295 (1955).